Final Report

To Tetra Tech EM, Inc.

On

Lead Speciation Studies of Herculaneum Soils and Household Dusts

by

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9th September 2002

1. Summary of Findings

Over 24,000 individual particles were characterized by CCSEM methods for the Herculaneum study, and over 10,000 were lead-bearing features. Lead concentrations are substantially enriched in the smaller size fractions of particles in both the soils and the household dusts. Source materials impacting the soils have largely lost their original characteristic microscopic attributes having undergone substantial chemical transformations. In the household dusts, little evidence is present for the direct impact of Slag materials, and only small amounts of Paint have been observed. The direct contribution of Concentrate materials to household dusts is generally ≤ 10% on a volume basis. Secondary lead phosphate formation in soils allows the determination of external soil contributions; these average about 30%. The remaining 60% of material derives from Road Dust, except for the attic dusts where 95-100% of the material appears to be from Road Dust.

2. Analytical Methods

A detailed description of the methods of sample preparation and of their characterization by CCSEM IPA methods can be found in Appendix I. The Herculaneum specimens detailed in this report have descriptions locations associated with their ID numbers as indicated in Table I, below.

Sample ID	Location	Type
H1	359 Station	Soil
H2	747 Mott	Soil
H3	747 Mott	Indoor carpet dust
H4	164 Joachim	Soil
H5	458 Thurwell	Soil
H6	458 Thurwell	Indoor dust
H7	329 Station	Soil
H8	329 Station	Indoor carpet dust
H9	329 Station	Attic dust
H10	710 Brown	Soil
H11	710 Brown	Indoor Carpet dust
H12	575 Main	Entry-way dust
H13	575 Main	Attic Dust
H14	575 main	Soil
H15	441 Thurwell	Soil
H16	Site	Slag
H17	Site	Concentrate
H18	Station & Main	Road dust

Table I. Sample ID, description and location of specimen collection.

3. Results

All of the results included in this report refer to the "fine" fraction of the specimen preparations. The "fine" fraction, for these purposes, refers to particles that have passed a **100 um** sieve. Most of the analytical interpretive effort has been associated with the lead-bearing particles; these are taken from the IPA (or CCSEM) results as features that showed at least 4% of the net x-ray count intensity (%XRI) as derived from lead. In this report, such particles are called **lead particles.**

3.1 Bulk Measures

3.1.1 Size Distribution. A normal quantile plot of the log transformed average diameter measure assessed the particle size distribution in the 15 environmental samples, plus 2 replicates. As a composite, these 17 analyses contained information on **26,455 individual particles**; their geometric mean diameter was 3.8 um (1.9 um – 7.5 um, one standard deviation). The normal quantile plot indicates that the population exhibits a joint lognormal distribution. Approximately 15 percent of the particles analyzed (4092) have an average diameter less than 1.8 um. However, if the lead-bearing particles are considered alone, the dataset contains **10,815 lead particles** of which 3327 (~31%) are smaller than 1.8um. The normal quantile plot for the lead particles is shown in Figure 1. The departure from a simple lognormal distribution is unusual and indicates there is a strong source for fine particles in the soils and household dusts of Herculaneum.
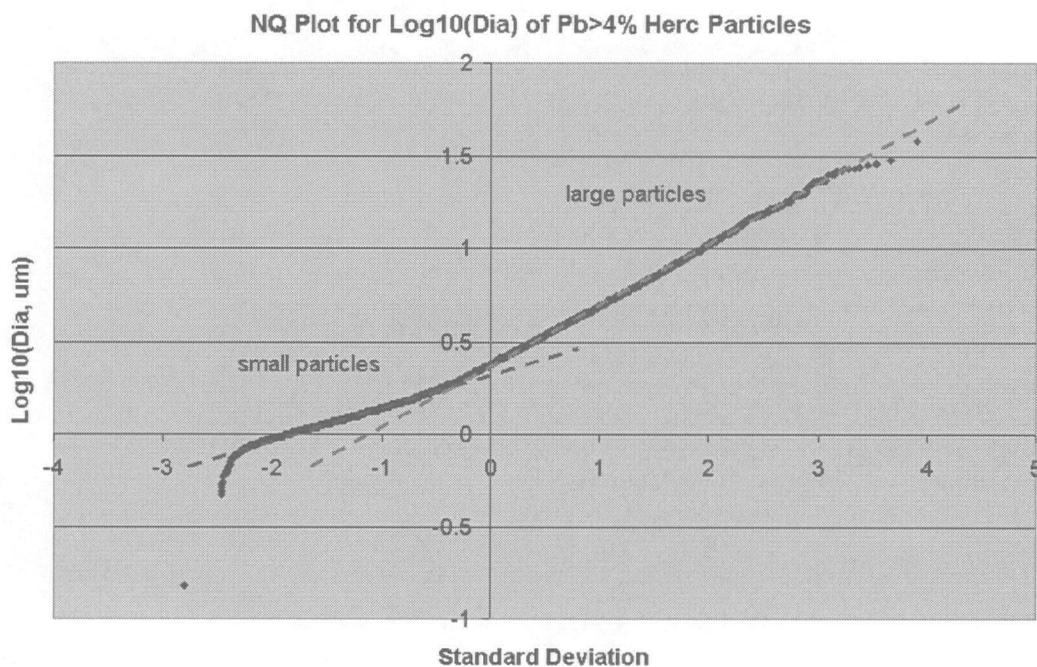

Figure 1. Normal Quantile (cumulative probability) plot of Log10(avgdia) of lead particles in Herculaneum soils, household- and attic-dusts.

3.1.2 Estimated Pb Content. The size of the particle and the distribution of relative x-ray intensity from the microanalysis, can be used to estimate the bulk composition of individual particles. When such estimates are summed over all analyzed features and corrected for the presence of matrix elements not analyzed (oxide corrections), the bulk elemental concentrations can be estimated (Johnson, et al, 1981). The approach is useful in the characterization of lead in soils, as a technique for interpreting the elemental associations in individual particles where x-ray detection limits the possible choice of phase distributions (Johnson and Hunt, 1995). The NIST SRM 2710 (Montana Soil) was analyzed for calibration purposes, and the weight percent elemental composition results are shown in Table II.

Element	IPA %	NIST %
Na	1.43	1.14
Mg	0.88	0.85
Al	6.66	6.44
Si	29.46	28.97
P	0.30	0.11
S	0.33	0.24
Cl	0.46	
K	3.90	2.10
Ca	1.53	1.25
Ti	0.32	0.28
Cr	0.08	
Mn	0.67	1.01
Fe	3.71	3.38
Ni	0.12	0.001
Cu	0.66	0.30
Zn	0.77	0.70
Cd	0.21	0.002
Pb	0.67	0.55

Table II. Calibration of the IPA procedure to bulk elemental values of NIST SRM 2710. A total of 3139 Montana Soil particles were prepared and analyzed under the conditions for the Herculaneum sample characterizations, and applied to elemental efficiency factors in the bulk composition calculations.

Using the SRM 2710 calibration, bulk lead concentrations were estimated for the Herculaneum samples. This was carried out for two particles size ranges (described later in section 3.3) covering all particles analyzed for each specimen as well as for the subset of particles that were lead particles. Results are shown in Table III, along with determination of the geometric mean particle sizes for the analyzed populations. Appendix II contains the SAS programs (drj.sas) used for the bulk composition estimates and (ghall.sas) used for the particle size computations.

Bulk Pb (%, IPA) In SAMPLE	All Sizes Total Sample	All Sizes Pb>4% Only	Dia <13um Total Sample	Dia <13um Pb>4% Only	Geo mean Size(um) Total Sample	Geo mean Size(um) Pb>4% Only
H1	1.3	8.7	1.8	8.3	4.29	3.09
H2	14	23	14	23	2.39	2.22
H4	4.0	12	6.1	13	3.40	3.00
H5	0.76	6.4	0.84	6.2	4.90	3.25
H7	6.0	14	8.8	14	2.79	2.45
H10	0.96	9.4	1.8	8.3	4.22	3.07
H14	1.1	7.8	2.0	8.0	4.12	2.67
H15	1.3	7.4	1.5	7.6	4.39	3.41
H9	5.6	12	6.1	13	2.58	2.10
H13	4.0	15	4.5	13	3.05	2.00
H3	4.5	17	9.5	24	2.33	1.80
*RH3	4.1	26	12	25	2.78	2.17
H6	0.75	4.5	1.0	7.4	3.66	2.25
H8	22	32	30	37	5.09	4.85
H11	0.98	17	3.9	20	3.11	2.23
H12	1	8	2	10	4.18	2.72
**RPH12	2	21	3	18	4.12	2.48
H16	2	16	19	30	2.62	2.14
*RH16	3	7	12	21	2.24	1.98
H17	53	67	53	67	1.61	1.56
H18	3	15	3	14	3.06	2.01
*replicate analysis	** replicate preparation					

Table III. Estimated Pb content (% by volume) and geometric mean particle size in Herculaneum specimens analyzed by IPA.

3.1.3 Proximate Elemental Associations in Herculaneum Lead Particles. Bivariate plots of elemental %XRI were constructed to determine whether unique, or characteristic, particle associations could serve to define tracer particle categories indicative of the various Herculaneum source materials. Characteristic plots are shown on the following pages; these have been used to derive partic le type classes for estimating the lead particle volume contributed by each to the environmental samples. Figures 2a-d relate to (H2) Soil, Figures 3a-d are for (H18) Road Dust, Figures 4a-d are for (H16) Slag, Figures 5a-b are summarize (H17) Concentrate, Figures 6a-b are for Metal/Oxide/Carbonate specimens and Figures 7a-b relate to the identity of barium sulfate particles. Appendix III contains such plots for all the specimens analyzed.
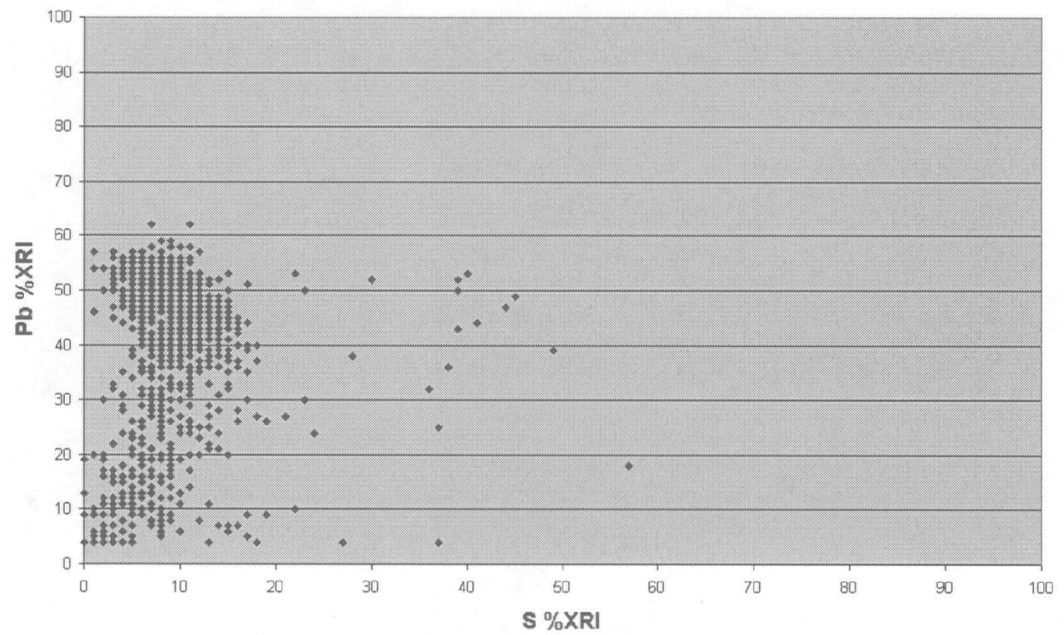
S vs Pb >4% in H2 Soil Particles

Figure 2a. S vs Pb in Soil H2 Lead Particles
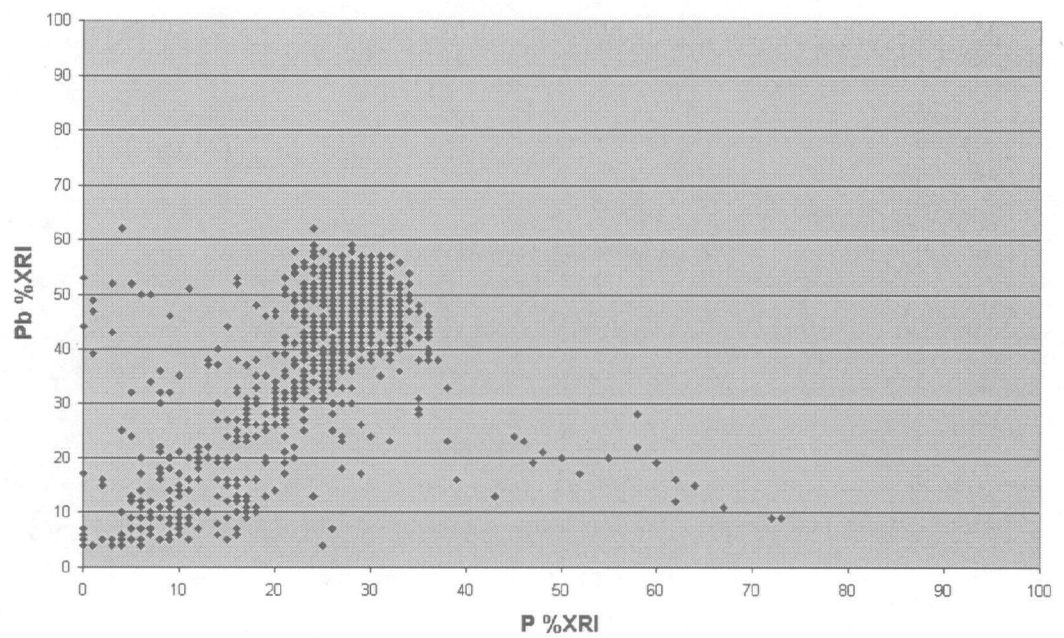
P vs Pb >4% in H2 Soil Particles

Figure 2b. P vs Pb in Soil H2 Lead Particles.

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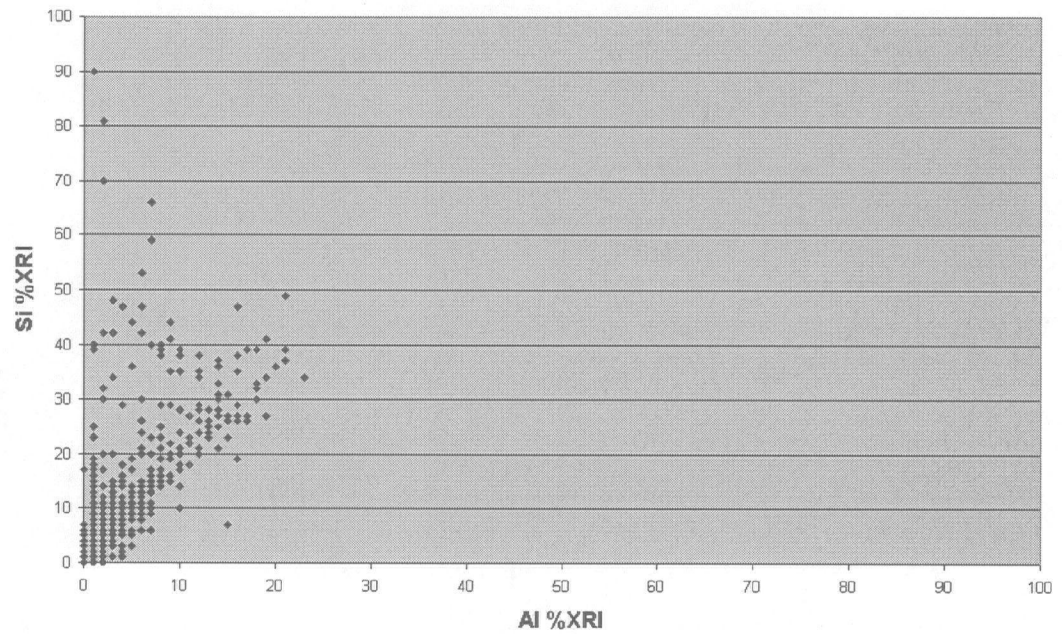**Al vs Si in Pb>4% H2 Soil Particles**

Figure 2c. Al vs Si in Soil H2 Lead Particles.
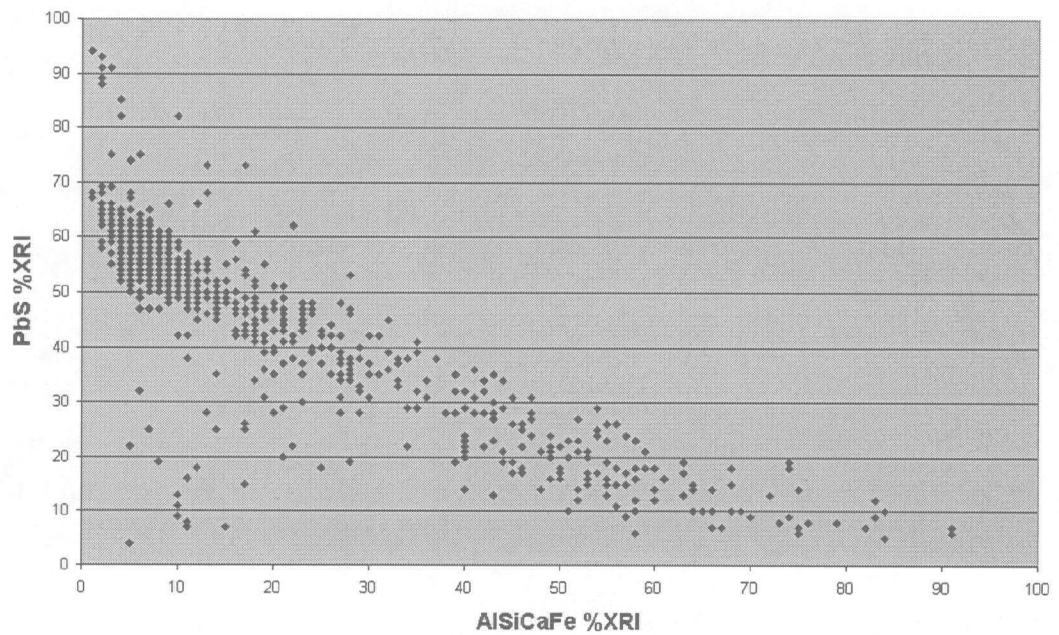
AlSiCaFe vs PbS in Pb>4% H2 Soil Particles

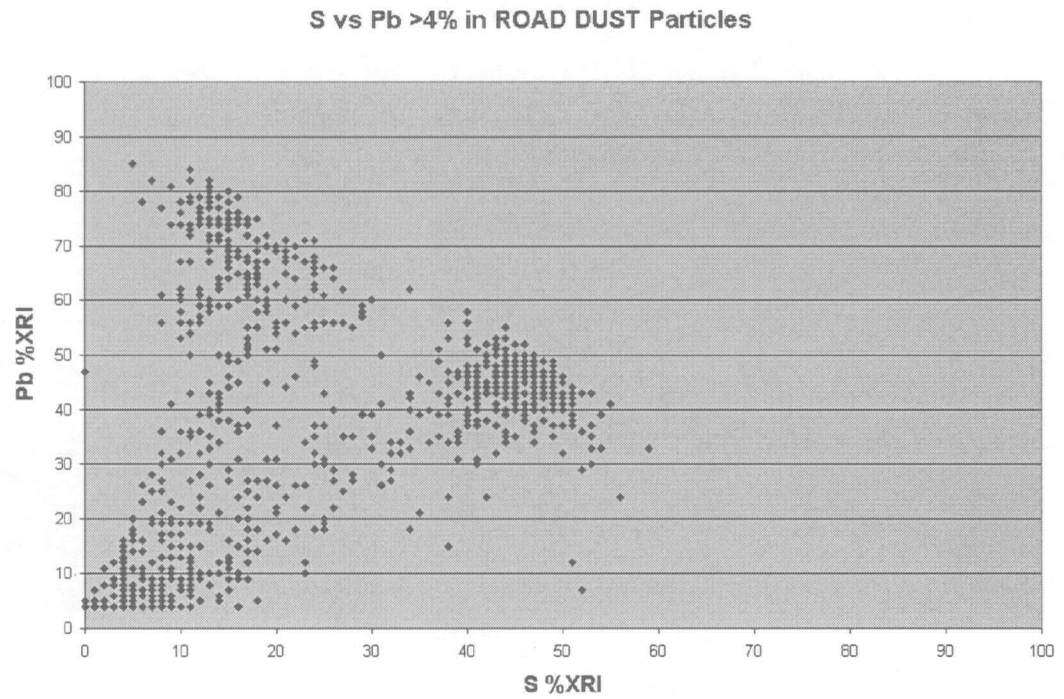Figure 2d. Al+Si+Ca+Fe vs Pb+S in Soil H2 Lead Particles.

S vs Pb >4% in ROAD DUST Particles

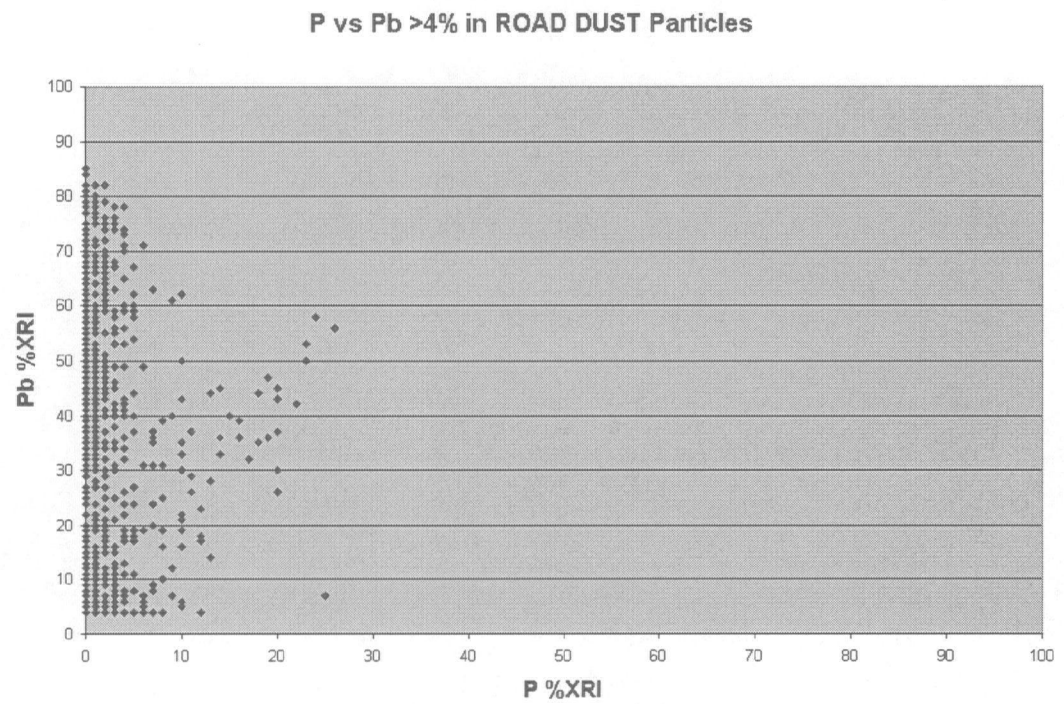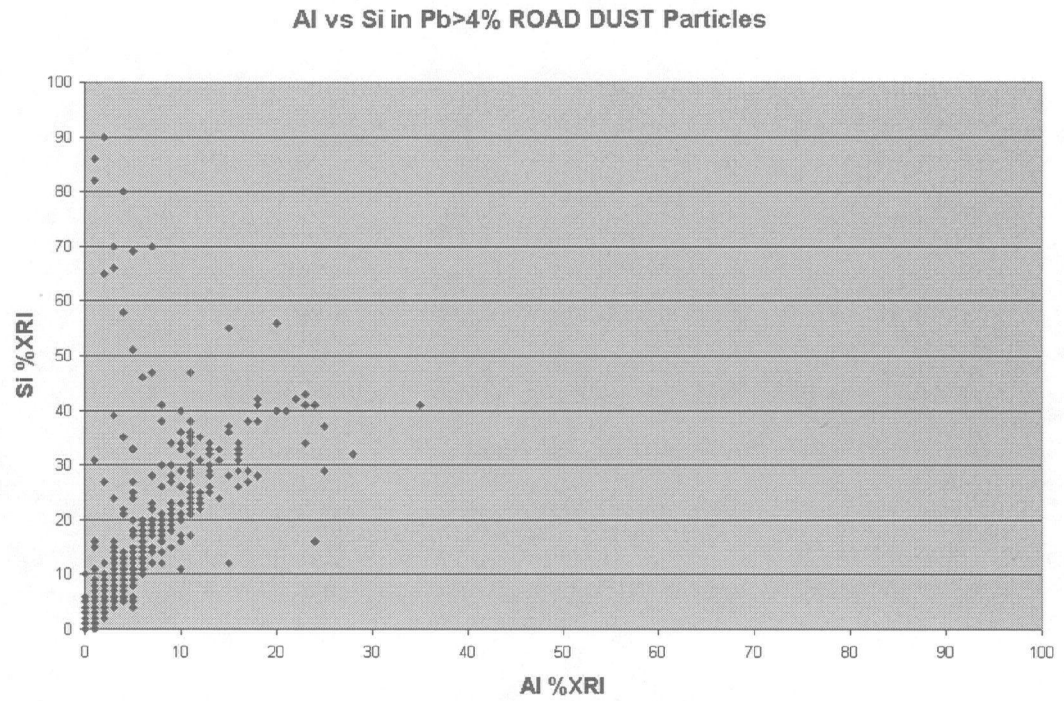Figure 3a. S vs Pb in H18 Road Dust Lead Particles.

P vs Pb >4% in ROAD DUST Particles

Figure 3b. P vs Pb in H18 Road Dust Lead Particles.

Al vs Si in Pb>4% ROAD DUST Particles

Figure 3c. Al vs Si in H18 Road Dust Lead Particles.

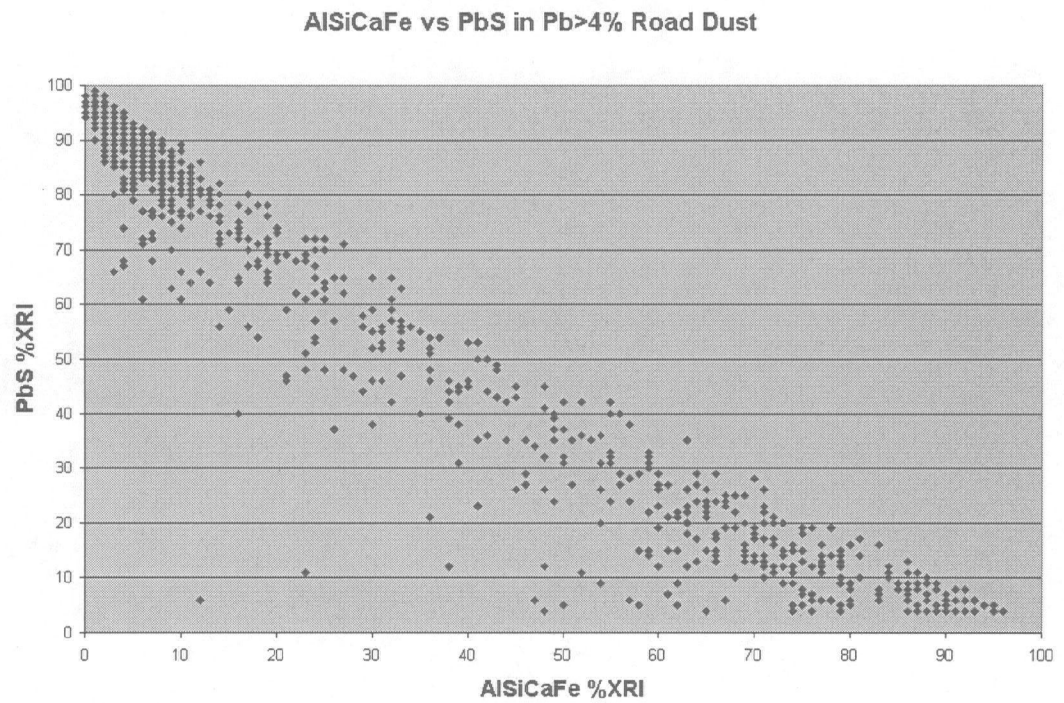**AlSiCaFe vs PbS in Pb>4% Road Dust**

Figure 3d. Al+Si+Ca+Fe vs Pb+S in H18 Road Dust Lead Particles.
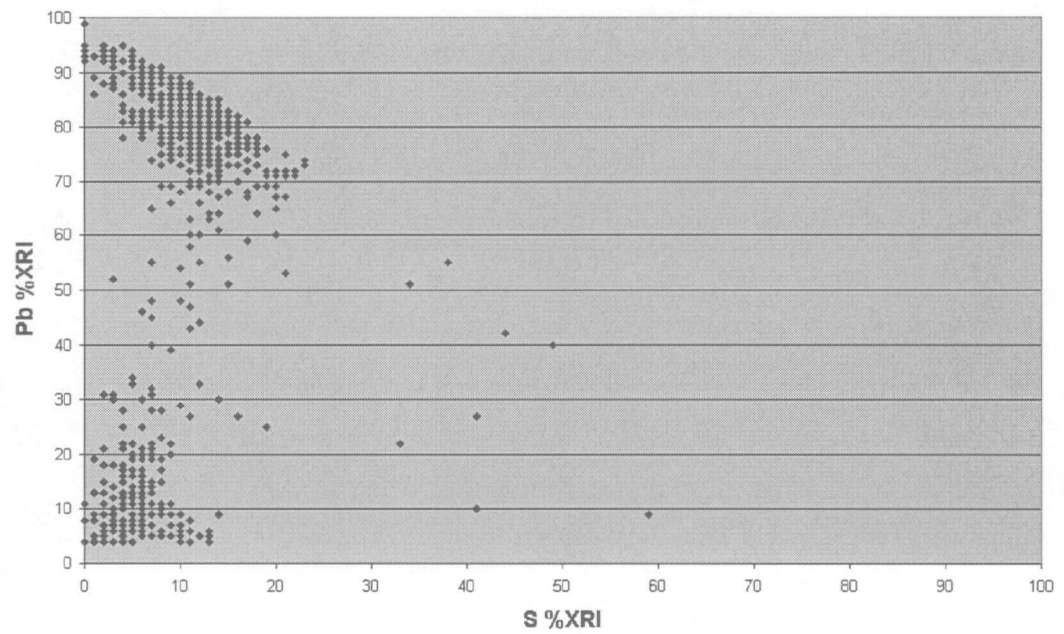
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S vs Pb >4% in SLAG Particles

Figure 4a. S vs Pb in H16 Slag Lead Particles.

Al vs Si in Pb>4% SLAG Particles

Figure 4b. Al vs Si in H16 Slag Lead Particles.
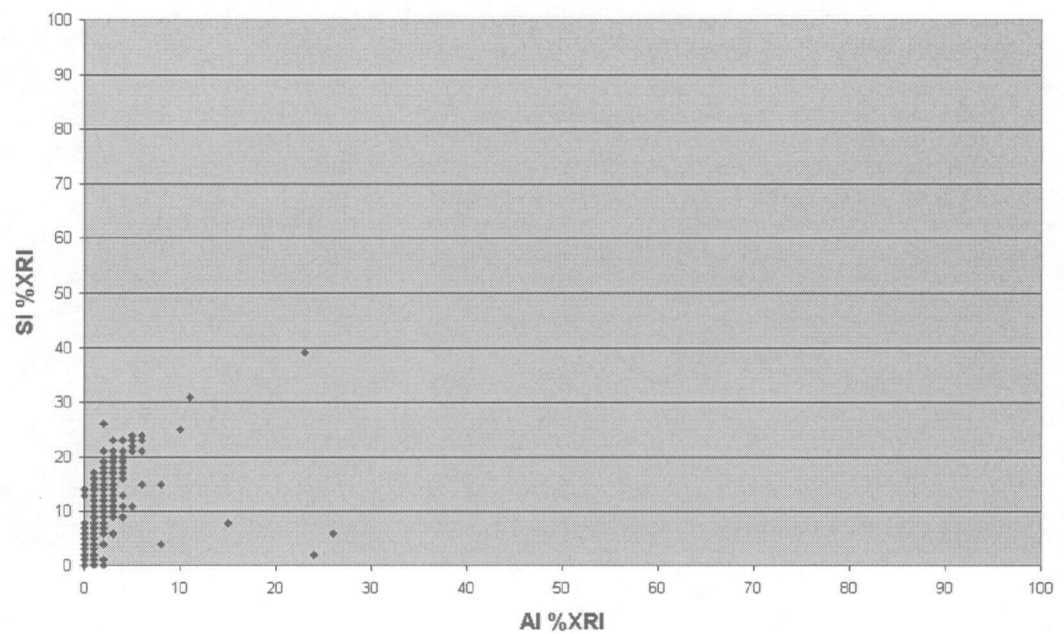
10

Si vs Ca in Pb>4% SLAG Particles
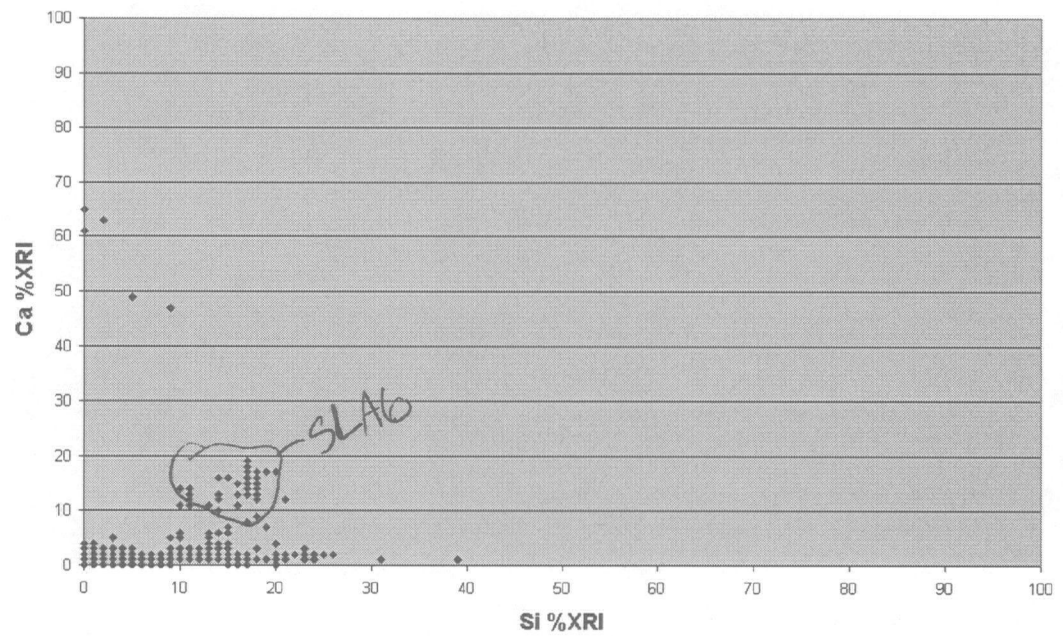
Figure 4c. Si vs Ca in H16 Slag Lead Particles.

Zn vs Pb >4% in SLAG Particles
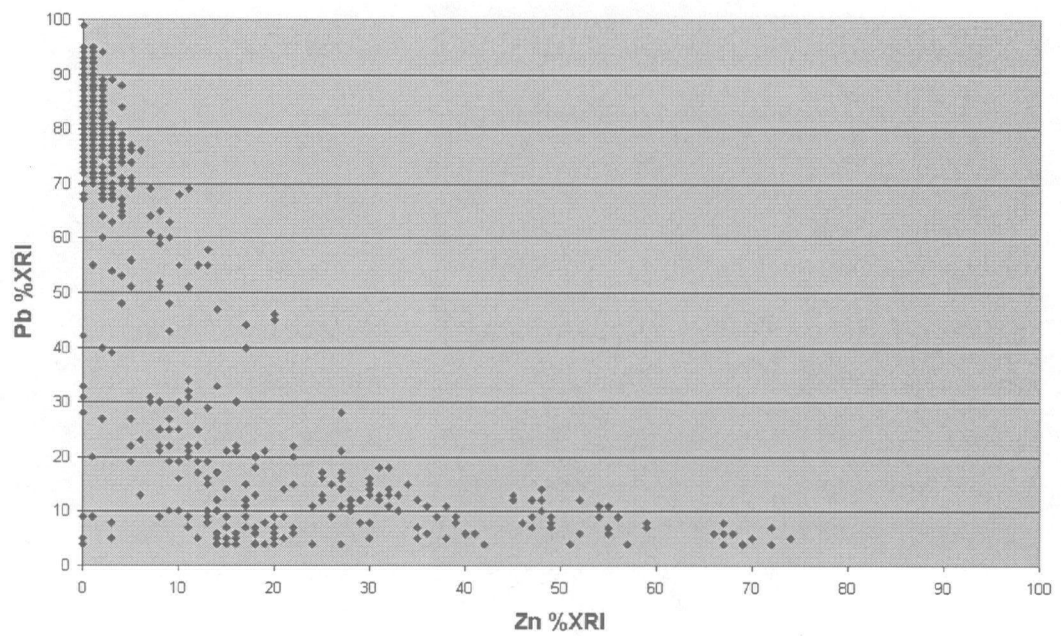
Figure 4d. Zn vs Pb in H16 Slag Lead Particles.

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S vs Pb >4% in CONCENTRATE Particles
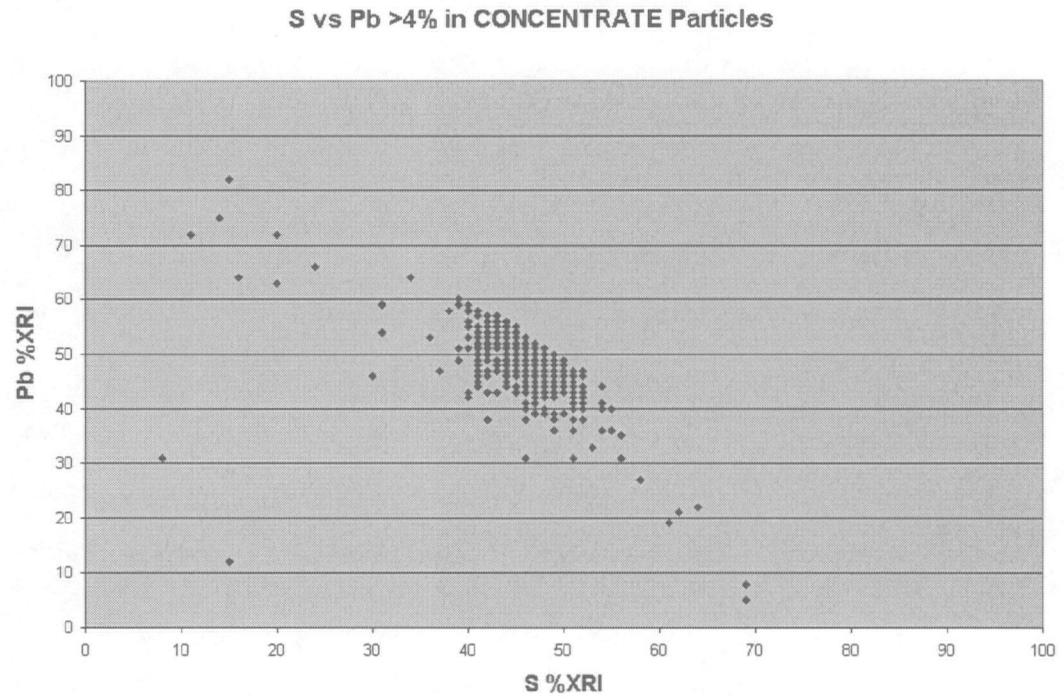
Figure 5a. S vs Pb in H17 Concentrate Lead Particles.

P vs Pb >4% CONCENTRATE Particles
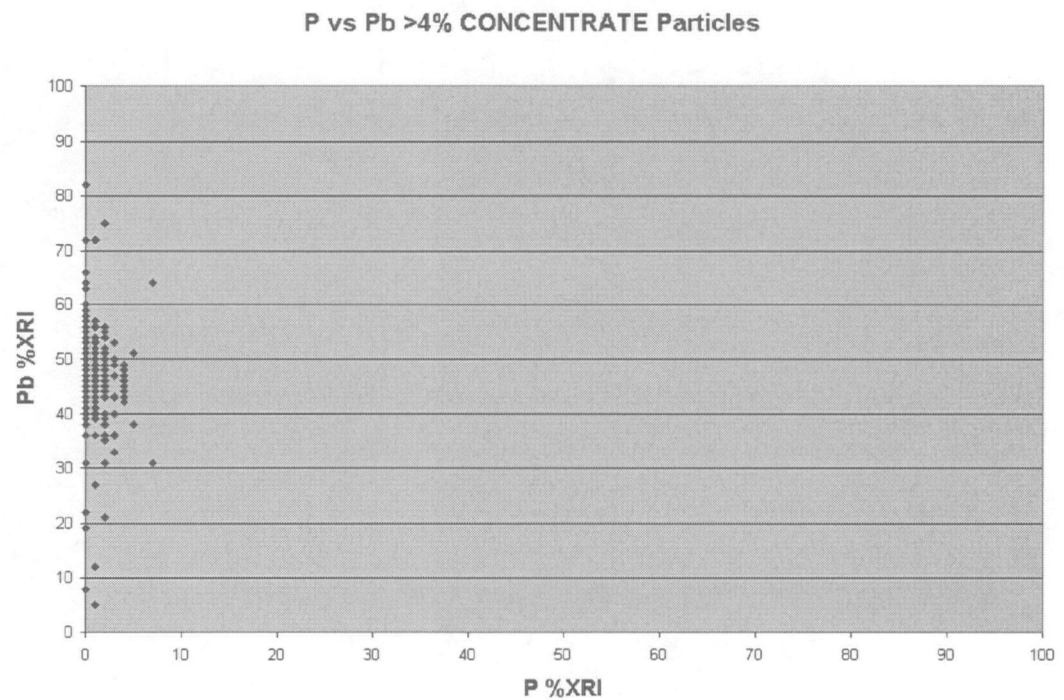
Figure 5b. P vs Pb in H17 Concentrate Lead Particles.
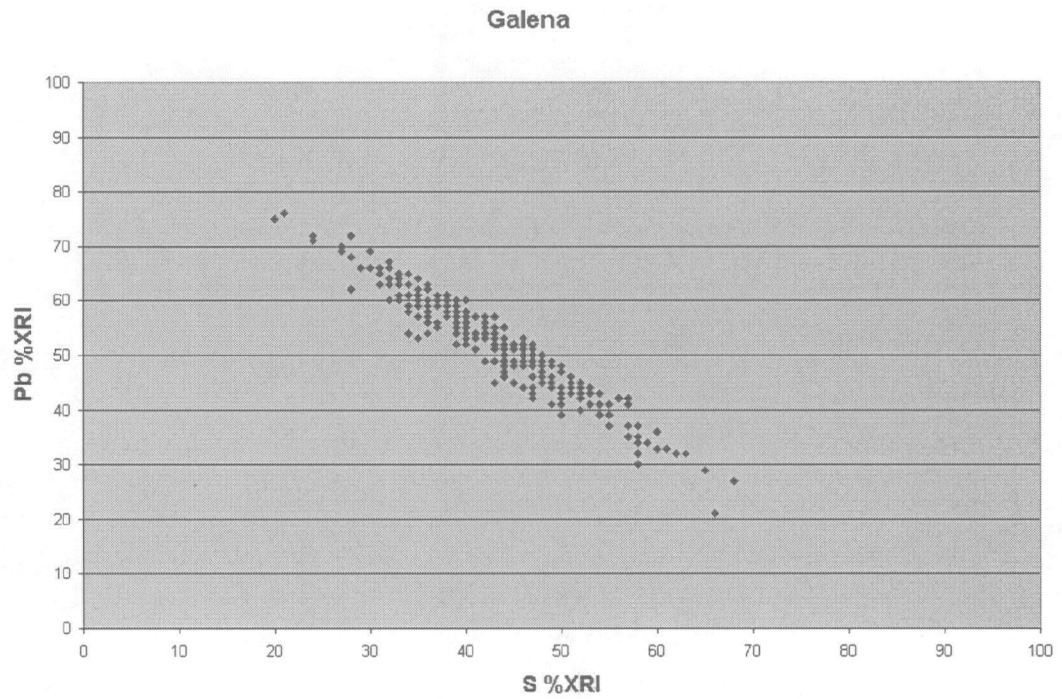
Galena

Figure 6a. S vs Pb in Galena sample.

S vs Pb in Metal, Oxide and Carbonate
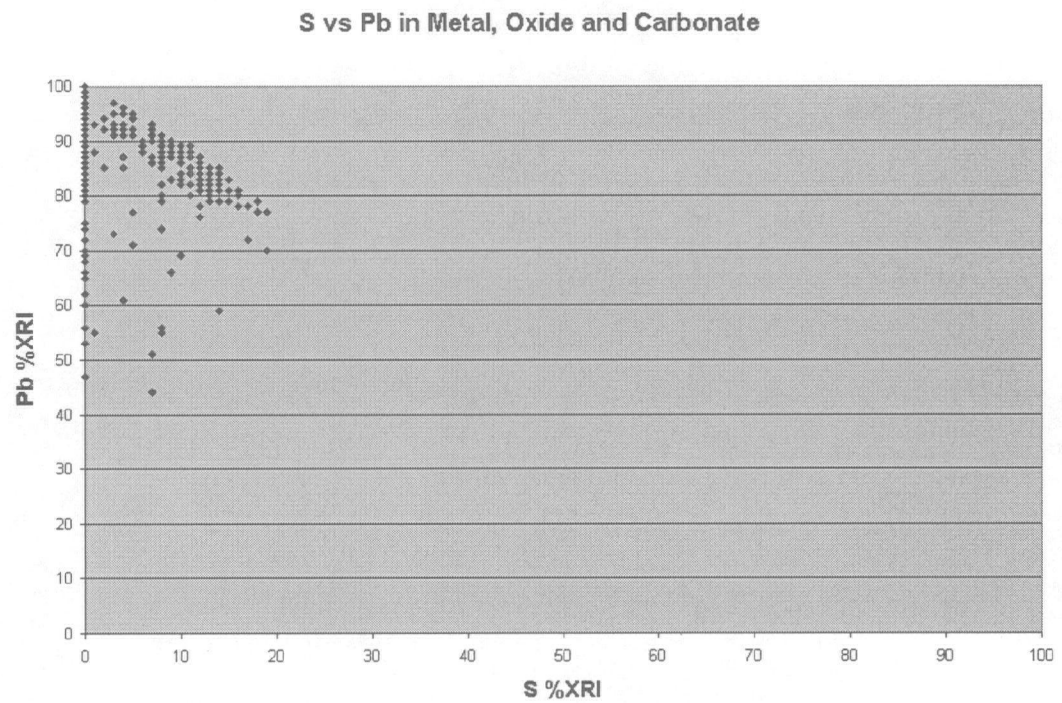
Figure 6b. S vs Pb in metal, oxide and lead carbonate samples.

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Ti vs S (BaSO4) in Herculaneum House and Attic Dusts
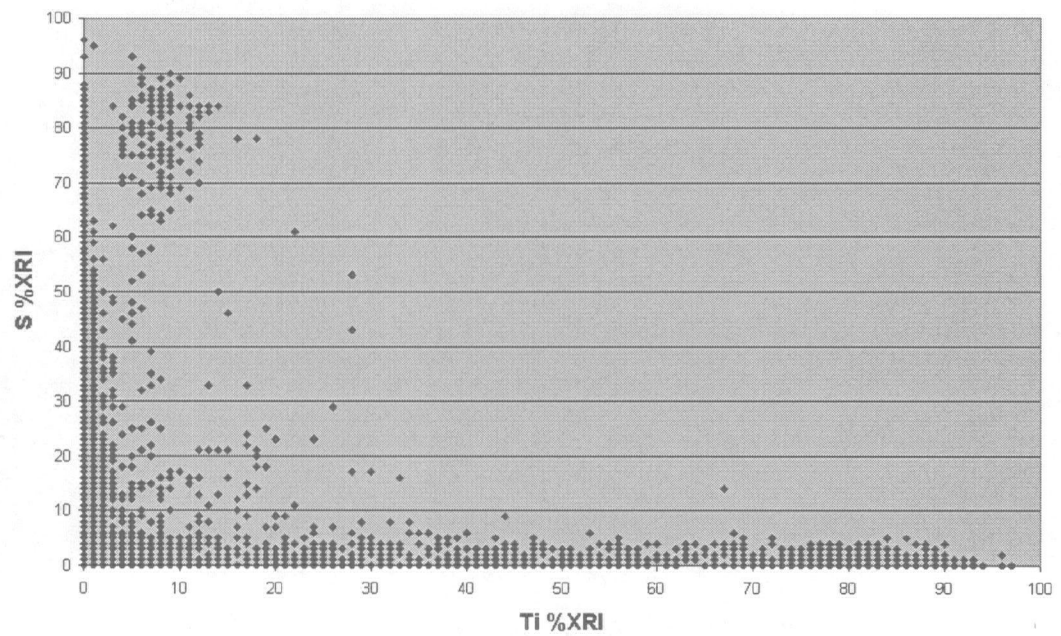
Figure 7a. Ti vs S (BaSO$_4$) in Herculaneum House and Attic Dust Particles.

Ti vs Pb > 4% in Herculaneum House and Attic Dust Particles

Figure 7b. Ti vs Pb in Herculaneum House and Attic Dust Particles

3.1.4 Lead Particle Types in Herculaneum Soils. The most characteristic features of the Herculaneum soils are the almost complete absence of Concentrate particles and the dominant presence of lead phosphate particle types. By comparison with the S/Pb association in Figure 5a, only a few Concentrate particles can be seen for Soil H2 shown in Figure 2a; a trend that is repeated for all 8 Herculaneum soil samples characterized. Figure 2b shows the strong presence of a P/Pb association centered at 50% Pb XRI and 30% P 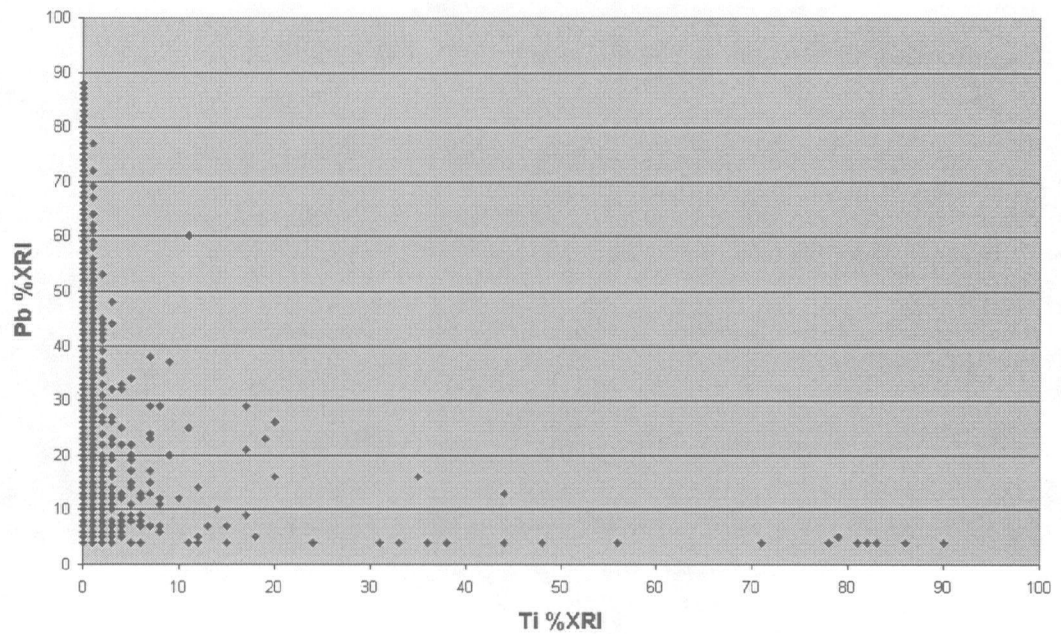XRI; the remaining XRI composition averages 10% for S and 10% for other elements variously. For these features, the 10% S XRI is probably an incomplete sulfur-lead x-ray overlap correction – note the sulfur x-ray presence in the analyses of lead oxide and carbonate particles as shown in Figure 6a. The lead phosphate features observed are likely due to *in situ* formation (Ruby, et al, 1994) and such soil transformations can easily obscure the characteristic features any original source material may have contained. However, little, if any, lead phosphate is observed in the other Herculaneum source materials, and thus **the P/Pb particle type can serve as a tracer for presence of soils in household dust samples**.

The presence of a strong Al/Si association in the soil samples (Figure 2c) cannot be easily distinguished from that of the Road Dust shown in Figure 3c. However, the S/Pb patterns for these two materials (Figures 2a and 3a) are quite different with the soil samples not showing many of the high lead (> 60 % Pb XRI) 'oxide' features. The same is true for the high lead features of Slag illustrated in Figure 4a. In both cases, these latter particle types are difficult to isolate from the reactive soil environment as they rapidly undergo repartitioning and adsorption to other types of soil particles (Johnson and Hunt, 1995). The 'tail' of the P/Pb plot in Figure 2b tending towards the plot origin, is fundamentally a continuous distribution with the alumino-silicate soil phases resulting from chemical and physical processes. This is illustrated in Figure 2d where the Pb+S %XRI plotted against the alumino-silicate %XRI accounts for most of the variability in the observations beyond the P/Pb association. **Slag, Road Dust and Concentrate contribution to the lead in Herculaneum soils cannot easily be distinguished by CCSEM IPA methods due to soil transformation processes.**

3.1.5 Lead Particle Types in Herculaneum Slag. The Slag specimen contained a substantial number of high lead features as shown in Figure 4a. It also portrayed a small Al/Si association, shown in Figure 4b, which is apparently of a different ratio to that found in the soils and Road Dust. As shown in Figure 4d, there is a significant presence of zinc in the Slag lead particles, and a small characteristic Si/Ca association plotted in Figure 4c. **Slag particles can be distinguished on the basis of a Si/Ca particle type that also contains Pb and Zn.** This group of features, however, is not a high proportion of the Slag features characterized, and, as with other source particle types, may undergo changes in the soil with loss of distinctive attributes.

3.1.6 Lead Particle Types in Herculaneum Road Dust. Figures 3a and 3b show that Road Dust lead particles show patterns for the presence of Concentrate features, but very little of the lead phosphate particle types. This suggests that the lead phosphate secondary mineral formation processes (potentially) taking place in the soils occurs to a much more limited extent in the Road Dusts. In fact, the presence of a small lead phosphate population here may simply reflect resuspension of adjacent soil particles. No Slag particles are observed, and (illustrated in Figure 3d) **the lead and sulfur together appear to form a continuous composition series with the alumino-silicate phases where in the lead is present either as a lead 'oxide' or a lead sulfide.**

3.1.7 Lead Particle Types in Herculaneum Concentrate. The Concentrate specimen analyzed shows the S/Pb relationship indicated in Figure 5a, and it shows no presence of a lead phosphate phase. The tight S/Pb group depicted in Figure 5a, as compared with that of the

Galena standard in Figure 6a, is a consequence of the small particle size exhibited by the Concentrate specimen (minimum ZAF attenuation of S x-rays). Note from Table IIII that it had the smallest size distribution of any of the study specimens, a geometric mean particle diameter under 1.6 um. If this accurately reflects the size distribution of the fine Concentrate particles, **their small size maximizes atmospheric transport potential and provides a high surface area/mass ratio for the (potential) secondary lead phosphate mineral formation in soils.**

3.1.8 Quantifying Lead-based Paint Particles. For small particle size ranges, characteristic multi-element associations with lead are present in diminished proportions because degradation of paint chips releases pigment particles from the binder. Empirically, one finds less 'lead paint' in the finer fractions of household dust (Hunt, et al, 1993). Particles originally derived from lead-based paints are mainly present as titanium dioxide, lead carbonate, barium sulfate and (occasionally) lead chromate. Barium is difficult to separate from titanium due to x-ray energy overlaps, and we did not include Ba in our element list for monitoring in this study. We did assess the presence of barium sulfate particles (noted visually from their spectra in some samples) by the distinctive Ti/S ratio of XRI, as shown in Figure 7a for the Herculaneum household and Attic Dusts. From analyses of the total analyzed particle populations, barium sulfate was found to be a maximum of 0.2% by volume (in H8). In our experience, **the association between titanium and lead has the highest probability of being a lead paint indicator;** the presence of lead paint particles so defined is shown in Figure 7b for the Herculaneum specimens. Very few lead paint particles were encountered in this study.

2. Descriptive Attribution for Lead Particles

3.2.1 Classification of Lead Particles. Based on the study of the elemental association detailed above, descriptive classification criteria were developed for the summary of the Herculaneum samples. Classification was carried out for lead particles only; that is for the subset of analyzed features with Pb %XRI equal to or greater than 4%. The criteria are listed below in the form of SAS **sub setting if** statements:

if $Ti \geq 4$ then class = Paint

if $Pb \geq 60$ then class = Oxide

if $Zn \geq 4$ and $5 < Ca < 20$ and $10 < Si < 25$ and class $\neq$ (Paint or Oxide) then class = Slag

if $20 < P < 40$ and $30 < Pb < 60$ then class = PbPhosphate

if $30 < S < 55$ and $35 < Pb < 60$ and class ne PbPhos then class = Concentrate

else class = Other

3.2.2 Computation of Lead Particle Type Contributions. Using the above criteria, the % volume-weighted contribution of each lead particle type was computed for each of the analyzed specimens. The computations are tabulated for two particle size ranges and serve as the basis for the source attribution estimates. Table IV presents data for the lead particle size range ≤ 13 um, and Table V for all sizes of lead particles in the fine fraction of the preparations.

% Volume in ≤ 13um	Paint	Oxide	Slag	PbPhos	Conc.	Other
H1	0.9	0.3	0	2.8	0.1	96.0
H2	3.3	0.1	0.3	40.7	0.1	55.6
H4	2.4	1.1	0.0	5.1	1.2	90.1
H5	3.0	0	0.0	3.7	0	93.3
H7	0.0	0	1.6	16.7	0.1	81.7
H10	1.0	0.0	0	6.1	0.1	92.8
H14	1.1	0	0.1	6.8	0	91.9
H15	2.6	0.2	0.1	2.0	0	95.1
H9	1.7	5.2	0.7	0.1	3.7	88.6
H13	1.5	1.9	0	0.3	9.7	86.6
H3	11.8	9.0	0.3	0.9	18.5	59.4
*RH3	8.4	5.8	0.4	6.9	16.3	62.1
H6	1.4	0.5	0	1.0	1.7	95.3
H8	0.2	15.6	0.2	5.2	29.6	49.0
H11	1.0	4.1	0	6.6	12.2	76.0
H12	1.4	0.1	0.1	1.1	2.6	94.7
**RPH12	0.5	3.7	0.1	4.6	8.4	82.7
H16	0	38.0	22.0	0	0.0	40.0
*RH16	0	20.8	21.1	0.0	0.0	58.1
H17	0	26.3	0	0	72.9	0.9
H18	0.3	4.9	0.6	0.3	6.7	87.2
*replicate analysis	**replicate preparation					

Table IV. Volume-weighted contribution made by defined particle types to the total lead particle volume contained in the size fraction with particle average diameter less than or equal to 13 um.

% Volume in ≤ 100um	Paint	Oxide	Slag	PbPhos	Conc.	Other
H1	0.7	0.2	0	2.2	0.1	96.8
H2	3.3	0.1	0.2	40.7	0.1	55.5
H4	1.6	2.9	0.0	3.4	0.8	91.3
H5	7.7	0	0.0	1.7	0	90.5
H7	0.0	0	1.3	14.0	0.1	84.6
H10	0.6	0.0	0	3.9	0.1	95.4
H14	0.4	0	0.0	4.4	0	95.1
H15	2.4	0.2	0.1	1.8	0	95.6
H9	1.3	4.0	0.6	0.0	2.8	91.3
H13	0.9	4.0	0	0.2	11.2	83.7
H3	6.3	3.5	0.1	0.2	8.1	81.9
*RH3	3.5	2.4	10.5	2.9	19.0	61.8
H6	0.6	0.2	0	0.4	0.8	97.9
H8	1.7	14.8	2.5	4.9	26.9	49.2
H11	0.8	3.5	0	5.6	10.5	79.6
H12	2.7	0.0	0.0	0.3	0.8	96.1
**RPH12	11.1	16.3	0.0	1.7	6.8	63.9
H16	0	14.5	38.6	0	0.0	47.1
*RH16	0	4.2	77.0	0.0	0.0	18.9
H17	0	26.3	0	0	72.9	0.9
H18	0.1	4.7	0.3	0.1	3.2	91.6
*replicate analysis	**replicate preparation					

Table V. Volume-weighted contribution made by defined particle types to the total lead particle volume contained in the size fraction with particle average diameter less than or equal to 100 um.

The tabulations shown for the volume-weighted contribution of defined lead particle types, above, include entries of 0 indicating that no particles were observed in these categories. Entries of 0.0 represent small contributions less than 0.05% by volume. Note three replicate specimens are included. House dust H3 and Slag specimen H16 were each analyzed on two occasions utilizing the same specimen preparation, but with different fields of view being characterized. One specimen, house dust H12 was characterized by analysis of two different specimen preparations. The replicate analyses indicate that some lack of clarity is present in the determination of source type 'finger prints'. This is particularly true for the entries in Table V relating to Slag and Concentrate in H3, Concentrate and Oxide in H12 and Slag in H16 (Slag). Most of this uncertainty is introduced by using the volume-weighted contributions since one or two large particles in a given analysis can distort the results; the resulting source apportionment estimates, however, are more realistic than those based on particle population alone. Data in Table IV were felt to be more consistent because of limiting the size range of particles in the summary to those 13 um in average diameter and below. However, the 'signatures in Table IV (size limited) and Table V have been used in subsequent steps of source apportionment.

3.3 Source Apportionment Estimates

No quantitative estimate of source contributions to the Herculaneum soils has been attempted; soil lead transformation processes have apparently been active. Whatever the original sources of the soil lead, its presence is now indicated by a lead phosphate phase. However, this particle type is largely absent from the other potential source materials analyzed, its presence in interior dust samples will be taken as indicative of the transport of external soil material, and quantified as such. The results of the present analyses (Table V) show the minor presence of paint in the soils at levels less than 10 % on a volume-weighted basis.

3.3.1 Method of Solution for Household and Attic Dusts. For the household dusts H6, H11 H12, and attic dusts H9 and H13, sources other than the direct deposition of Paint, Oxide, Slag or Concentrate dominate the particulate lead fraction and for dusts H3 and H8, they comprise a minimum of about 50% contribution. **The apportionment computation we undertake here assumes that the 'Other' lead in Table IV is derived from some mixture of the general road dust category and the local external soil. Thus, we formulate a closed solution in which the fraction of external soil contributed is determined by dilution of the local PbPhos particle type and the remainder ascribed to Road Dust.**

Variability in the source signatures does not justify an exhaustive mathematical treatment for determining a quantitative apportionment solution within the stated assumptions. The results were obtained largely by inspection of the summary results in Table IV by employing the steps detailed below and were rounded to the nearest 5%. Reference below to local soil (step 2) relates to the soil matched to the address of the House Dust samples as delineated in Table I of the Methods Section.

Steps for obtaining the closed end apportionment by inspection using Table IV entries for (example) House Dust H8 and the matching local soil H7:

1. Paint was determined directly from the Table IV volume estimate
   { Paint % = 0.2, therefore neglect **0% Paint final** }
2. Soil fraction = (Dust PbP/local Soil PbP)
   { 5.2/16.7 = 0.3, or **30% Soil in final** }
3. Initial Road Dust (RD) fraction = (1.0 – Paint – Soil)
   { (1.0 – 0.0 – 0.3) = 0.7 }
4. Initial RD fraction times 6.7% estimates RD Concentrate
   { 0.7 * (6.7%) = 5% Concentrate from RD }
5. Observed Concentrate – (RD Concentrate) = Direct Concentrate
   { (29.6% observed – 5% from RD) = **25% Direct Concentrate in final**}
6. Final RD contribution = 100 –(% Paint + % Soil + % Direct Concentrate)
   { 100 – (0% Paint + 30% Soil + 25% Direct Concentrate) = **45% RD in final** }

3.3.2 Source Apportionment Results. Tables VI and VII, below, summarize the descriptive, closed solution, source apportionment estimates for the 7 household dust samples with 2 replicates and the 2 attic dust samples. Entries, rounded to the nearest 5%, are estimated for the volume-weighted contribution of the 4 sources: Paint, Concentrate, Soil and Road Dust.

Sample	Paint	Concentrate	Soil	Road Dust
H3	10%	15%	5%	70%
RepH3	10%	10%	20%	60%
H6	--	--	30%	70%
H8	--	25%	30%	45%
H11	--	15%	85%	--
H12	--	--	20%	80%
RepH12	--	--	70%	30%
H9	--	--	--	100%
H13	--	--	5%	95%

Table VI. Estimated source strengths for the apportionment of fine lead particles in Herculaneum household and attic dusts, limited to the size fraction of 13 um and less.

Sample	Paint	Concentrate	Soil	Road Dust
H3	5%	5%	--	90%
RepH3	5%	15%	5%	75%
H6	--	--	25%	75%
H8	--	25%	35%	40%
H11	--	10%	90%	--
H12	5%	--	10%	85%
RepH12	10%	5%	40%	45%
H9	--	--	--	100%
H13	--	--	5%	95%

Table VII. Estimated source strengths for the apportionment of fine lead particles in Herculaneum household and attic dusts, limited to the size fraction of 100 um and less.

3.3.3 Discussion of Apportionment Result Validity. The general results of the apportionment seem to fit a pattern wherein Paint contributes < 5%, Concentrate contributes 5-10%, Soil contributes 20-30% and Road Dust contributes 50-60% of the lead particle volume found in the household dusts. Similar high proportions of external soil/dust contribution to indoor dusts have been observed elsewhere (Hunt, et al, 1993; Sterling, et al, 1998). For the attic dusts, 95-100 percent of the contribution comes from Road Dust. For both of these ambient sample types, the presence of Slag materials is nil. Source materials lose their microscopic

identity in the chemically active soil environment with the formation of a distinctive secondary lead phosphate mineral phase attributable almost solely to the soils. Most of the lead present in the soils and the road dusts is associated with an alumino-silicate matrix, making it distinctive from other potential source materials such as paint or direct smelter emissions, difficult to resolve one from the other.

The descriptive power of the apportionment approach shows good reproducibility in the determination of small amounts of Paint and Concentrate source materials in the ambient samples, and consistently indicated the lack of any significant contribution from Slag. For separation of Soil and Road Dust contributions, uncertainty is higher, as noted by the large range of values for Soil H12 in Tables VI and VII. The absolute variability of PbPhos (Tables IV and V) is not great, but as the determination of Soil or Road Dust is dependent upon the value of a ratio of tracer particle types, greater variation is experienced. Knowing this, after the fact, indicates that future work with this technique should characterize a higher number of replicate specimen preparations and seek to increase the total population of lead particles analyzed. Calculating the apportionment results for a restricted size range, ≤ 13 um average diameter, was thought to be helpful in restricting the variability of results influenced by a few outliers in the size distribution. Noting the comparative results from Table VI and VII shows this not to be the case.

The particle sizes in the Herculaneum samples are unusual in their joint lognormal distribution; a small size range apparently exists with a size less than about 2 um. In Figure 1, this cut point (change of slope) is at about 1.8 um. The percent lead particle volume distribution is shown below for the classes of particles used in the apportionment

Particle Type	Relative Volume in ≤ 1.8 um	Relative Volume in ≤ 100 um
In Herculaneum Soils		
Paint	0.8	2.0
Oxide	2.9	3.6
Slag	0.2	0.7
PbPhosphate	76.5	5.5
Concentrate	2.2	5.9
Other	17.4	82.4
In Herculaneum Dusts		
Paint	0.5	4.1
Oxide	6.0	4.6
Slag	0.2	0.9
PbPhosphate	9.4	0.8
Concentrate	54.3	6.8
Other	29.5	82.6
In Herculaneum Sources		
Paint	0.2	0.0
Oxide	53.1	7.9
Slag	0.4	54.1
PbPhosphate	0.2	0.0
Concentrate	30.9	1.1
Other	15.2	36.9

Table VIII. Relative volume of lead particle types in different size fractions of samples.

This compilation illustrates several important results:

1. For the Herculaneum source materials, 'Oxide' and Concentrate particle types dominate the small size class. The small oxide particles are not distinctive in CCSEM procedures and are common to a variety of sources including paints and smelter emissions. Such particles would aggregate easily with alumino-silicate materials of Road Dust forming the composition series shown in Figure 3d. In the soil environment, they would react quickly through a variety of potential chemical transformations.

2. For the passive chemical environment of the household dusts, above, concentrate particles contribute a majority of the lead particle volume in the ≤ 1.8 size range. This material is apparently available for direct transport to the interior household environment, or more likely, as the apportionment results show, through resuspension of Road Dusts.

3. For the Herculaneum soils, the PbPhosphate particle type dominates the small particle size range material. It seems likely that the origin of this material is the Concentrate, but further investigations would be required to support such a hypothesis. Equally, it seems unlikely that the wide distribution of this secondary mineral phase in the soils could be attributed to weathered lead-based paints, as there is insufficient supporting evidence to indicate such a process has occurred widely.

4. High amounts of lead in very small particle size ranges can explain the unusually high bulk lead estimates (Table III) for the Herculaneum specimens. There is a very large enrichment is the smaller size ranges, and this fact needs careful consideration in any discussions of potential health effects implications.

4. References

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